

COATINGS. ENAMELS

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USE OF TECHNOGENOUS MATERIALS IN PRODUCTION OF SILICATE COATINGS FOR PROTECTION OF HIGH-ALLOY STEELS

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Silicate coatings have been synthesized on the basis of metallurgical waste for the purpose of protecting high-alloy steel from corrosion under heat treatment. The main properties of the coatings are described.

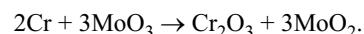
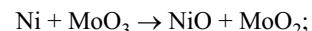
The problem of protecting high-alloy steel from oxidation under high temperatures using glass ceramic coatings attracts much attention [1]. This protection can be provided not only by traditional raw materials, but also by available industrial wastes generated by various factories and local silicate materials.

The present study considers the possibility of using electrothermal phosphor slag from the Fosfor JSC and slag generated by a slag-fuming set used in lead production. The chemical compositions of the slag samples taken for experiments [2] were as follows (wt.-%): 41.23 SiO₂, 47.55 CaO, 2.87 Al₂O₃, 3.37 MgO, 0.69 Fe₂O₃, 2.29 P₂O₅, 0.03 SO₃, and 2.03 F for electrothermal phosphor slag; 25.12 SiO₂, 13.80 (CaO + MgO), 7.50 Al₂O₃, 40.20 Fe_{tot}, 0.50–0.70 CuO, 1.30–2.20 ZnO, 0.20 PbO, 0.90 SO₃, and 9.57 other for lead slag from the slag-fuming unit.

The frits were melted at the Gazalkent Oina glass factory in an electric glassmelter with silite heaters, in platinum crucibles at temperatures between 1400 and 1500°C. After holding for 1 h, the melts were poured into water for granulation. All frits were properly melted and had satisfactory homogeneity. The results of the chemical analysis of the frits, which was carried out in industrial conditions, are given in Table 1.

The frits were crushed in porcelain mortars. Next, 5% Tolebiiskoe clay and water were added to the resulting enamel slip. The samples of complex-alloy steels 14KhN3MA and KhVG were preliminarily degreased, then immersed in the slip, and dried. The heat treatment was carried out in a muffle furnace at temperatures 700, 750, 800, 850, 900, 950, and 1000°C with 5 min holding. After heat treatment, the exterior appearance of different coated steel substrates differed significantly, depending on the coating composition.

A specific feature of high-alloy steels is the fact that their composition, in addition to standard components (carbon, silicon, manganese, sulfur, etc.), also includes tungsten and molybdenum (up to 10 wt.-%). It was found that in heat treatment, the surface of the sample gets rapidly oxidized, which is accompanied by the formation of scale with a rather loose structure. The acceleration of oxidation is presumably due to the formation of molybdenum and tungsten oxides and their subsequent reactions with steel components according to the following scheme:



Similar results were obtained in [3].

The developed coatings provide adequate protection from oxidation for high-alloy steels under heat treatment.

The specifics of vitreous coatings consists in their capacity for modification during their formation and the emer-

TABLE 1

Compo- sition	Mass content, %						
	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	Na ₂ O	others
1	71.35	2.65	10.70	0.85	4.90	7.55	2.00
2	68.00	2.05	10.65	1.00	3.90	11.55	2.85
3	68.05	2.00	11.00	1.10	3.80	11.90	2.15
4	70.80	3.15	12.60	0.90	2.35	8.50	1.70
5	69.50	3.50	14.05	0.65	2.40	7.60	2.30
6	70.05	2.35	6.15	9.40	1.50	9.15	1.40
7	69.70	3.90	8.40	9.60	2.75	3.40	2.25
8	58.00	4.50	9.50	17.05	4.85	3.50	2.60
9	69.85	3.30	8.05	8.55	2.45	5.90	1.90
10	61.05	7.05	10.90	8.70	3.90	6.00	2.40

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TABLE 2

Compositions	Density, g/cm ³	TCLE, 10 ⁻⁷ K ⁻¹
1	2.3050	71.25
2	2.2882	93.23
3	2.2362	95.06
4	2.3140	78.24
5	2.3550	76.01
6	2.4387	75.41
7	2.4594	50.55
8	2.4658	61.48
9	2.4637	63.00
10	2.4441	72.13

gence of crystalline phases. The volume macrocrystallization and the uniform distribution of the finely disperse crystalline phase ensure an improvement of the service parameters of protective coats, i.e., the gas permeability decreases, and the density and viscosity of the coatings grow. The improvement of properties is due to the formation of crystal phases distributed inside the protective coating (β -cristobalite, α -tridimitite, ferrous spinels, etc.) and a decrease in the vitreous phase content.

Our purpose was to select a composition with a low TCLE for the production of ferrous-slag glasses which would have sufficiently good properties at high temperatures (Table 2). The crystallization of the substrate and the content of alkaline oxides in the initial glass compositions made it possible to obtain coatings with a tendency to crystallize.

Compositions 7 and 8, studied by the mass crystallization method [4], had a continuous thick crust on the surface, with partial extension of the crystals into the material volume, whereas crystallization in compositions 9 and 10 expanded throughout the volume. Apparently, a high content of

iron oxides in the lead production slag results in the high propensity of these compositions to crystallize. The x-ray phase analysis corroborates this conclusion, as the x-ray patterns exhibit the presence of iron-bearing crystalline phases: hedenbergite, magnetite, and hematite.

A low TCLE imparts an important property to the coatings: they are capable of crumbling spontaneously off the surface of the article when air-cooled after heat treatment, thus freeing the light-colored unoxidized high-quality surface of the metal. In this way, compositions 7–9, with low TCLE, being deposited on the considered steel samples, easily fell off the surface when cooled in air after heat treatment, without any residual traces.

The use of protective technological coatings in production does not require sophisticated equipment, and the implementation of this method is possible in hot metal working technologies, including extrusion, forging, stamping, etc.

The developed protective coat compositions (7–9) based on recycled waste and local freely available silicate material can be recommended to prevent oxidation and decarbonization of high-alloy steel in the course of thermal treatment.

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